TOPIC : HYDROCARBONS
EXERCISE # 1

SECTION (A)

1. Boiling point $\propto$ surface area of the molecule,

7. $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - O.Na + NaOH + CaO \xrightarrow{\Delta} \underset{\text{ethane}}{CH_3 - CH_3} + Na_2CO_3$

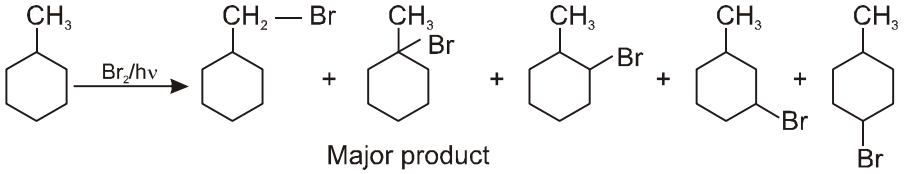
10. $LiAlH_4$, Na/dry ether and R_2CuLi are convert alkyl halide into alkane.

16. Halogenation of alkanes is an example of free radical substitution reaction

19. $CH_4 \xrightarrow[Cl_2]{h\nu} CH_3Cl \xrightarrow[-HCl]{h\nu/Cl_2} CH_3Cl_2 \xrightarrow[-HCl]{h\nu/Cl_2} CHCl_3 \xrightarrow[-HCl]{h\nu/Cl_2} CCl_4$

21. $\overset{(1)}{CH_3} - \underset{\displaystyle CH_3}{\overset{(2)}{\underset{|}{CH}}} - \overset{(3)}{CH_2} - \overset{(4)}{CH_2} - \overset{(5)}{CH_3}$

22. For photochemical bromination reactivity of hydrogen atom is 3°H > 2°H > 1° H.



Major product

$\therefore$ Ans. is (3)

23. Iodination of an alkane is carried out in presence of HNO_3 or HIO_3

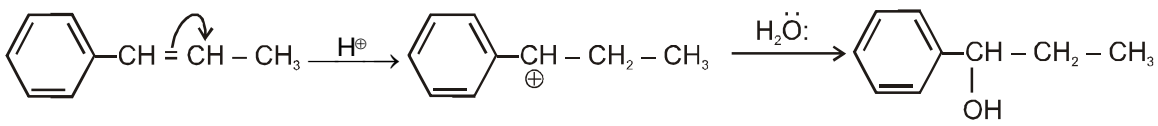
24. $\underset{\displaystyle C_3H_4}{\overset{\displaystyle H}{\underset{|}{\overset{|}{CH_3 - C^* - CH_2.CH_3}}}} = C_7H_{16}$

$12 \times 7 + 16 \times 1 = 100$

SECTION (B)

2. $CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{\overset{Br}{\underset{|}{\overset{|}{CH_2 - CH_2}}}}$

3. Bromination is anti addition.

4. 

5. $CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2+H\overset{\delta-}{O}-\overset{\delta+}{Cl} \longrightarrow CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

6. (1) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow[h\nu]{Br_2} CH_3-\underset{CH_3}{\underset{|}{C}}-Br + CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-Br$

Major 3° Alkyl halide; Minor

(2) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow[\text{Peroxide}]{H-Br} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-Br$

1° Alkyl halide

(3) $(CH_3)_2CH-CH=CH_2 \xrightarrow{H^{\oplus}} CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{\oplus}{C}H-CH_3 \xrightarrow[\text{Shiffting}]{1,2\ H^{\ominus}} CH_3-\underset{CH_3}{\underset{|}{\overset{\oplus}{C}}}-CH_2-CH_3$

$\xrightarrow{Br^{\ominus}}$ 3° Alkyl halides $CH_3-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_2-CH_3$

So, answer is (4)

12. Peroxide effect is observed only with HBr

14. $CH_3-CH=CH_2+H-Br \xrightarrow{H_2O_2} CH_3-CH_2-CH_2-Br$

SECTION (C)

1. General fomula C_nH_{2n-2} represents alkynes

2. $CH_3-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_3 \xrightarrow{Zn\ dust} CH_3-C\equiv C-CH_3$ (But -2-yne)

3. $2Mg^{+2}(\bar{C}\equiv C-C^{3-}) \xrightarrow{H_3O^+} Mg(OH)_2 + CH\equiv C-CH_3$ (Propyne)

5. Most Acidic hydrogen is present in ethyne.

7. $CH_3-C\equiv C-CH_3 \xrightarrow[\text{Lindlar's}]{(1)\ H_2/Pd/CaCO_3}$ Cis $\xrightarrow[\text{Anti addition}]{Br_2}$ (dℓ) - 2, 3 dibromo butane

8. $H-C\equiv C-H+HO-Cl \longrightarrow \underset{Cl}{\underset{|}{CH}}=\underset{OH}{\underset{|}{CH}} \xrightarrow{HOCl} Cl_2CH-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}-O-H \xrightarrow{-H_2O} Cl_2CH-\overset{H}{\overset{|}{C}}=O$

unstable

9. 1-Butyne can be converted into 1-bromo-1-butene by antimarkownikoff. Addition of H-Br in presence of peroxide.

10. $CH_3 - CH_2 - C \equiv C - H \xrightarrow{HBr} CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{C}} = CH_2 \xrightarrow{HBr} CH_3 - CH_2 - \underset{\displaystyle Br}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}} - CH_3$

11. $H-C\equiv C-H + H_2O \xrightarrow{Hg^{+2}} CH_2 = \underset{\displaystyle OH}{\underset{|}{CH}} \rightleftharpoons CH_3CHO.$ Ans is (1).

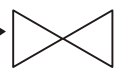
13. 1-butyne and 2-Butyne can be distinguish by ammonical silver nitrate solution.

SECTION (D)

2. Isomerization of an alkane may be carried out by using anhyd. $AlCl_3$ at 300ºC in presence of a trace of alkyl halide or alkene

EXERCISE # 2

1. $(CH_3)_2CH - CH_2 - CH_2 - CH(CH_3)_2$ syntheized in good yield in wurtz reaction

2. $BrCH_2-C(CH_2Br)_2-CH_2Br \xrightarrow[\text{ether, heat}]{Na}$ 

3. CH_3-CH_2COOH →
- $\xrightarrow{HI / Red\ P} CH_3CH_2CH_3$
- $\xrightarrow[\Delta]{NaOH / CaO} CH_3CH_3$
- $\xrightarrow{NaOH\ (electrolysis)} CH_3CH_2-CH_2CH_3$

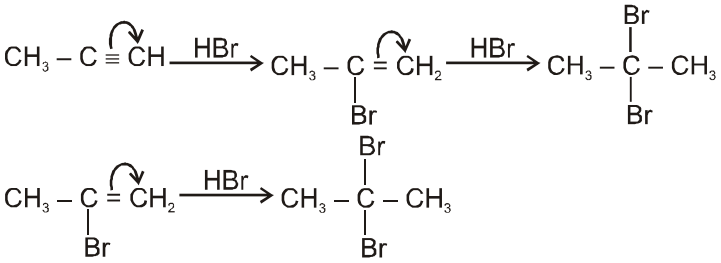
5. $CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{h\nu, Br_2} \underset{\displaystyle Br}{\underset{|}{CH_3 - CH - CH_2 - CH_3}}$ (2-bromobutane) $+$ $Br - CH_2 - CH_2 - CH_2 - CH_3$ (1-bromobutane) (equimolar ratio)

6. $H_3C - CH_2 - \underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3 \xrightarrow{Cl_2/h\nu} CH_3 - \underset{\displaystyle Cl}{\overset{*}{\underset{|}{CH}}} - \underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3$

$CH_3 - CH_2 - \underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3 + CH_3 - CH_2 - \underset{\displaystyle *}{\underset{|}{CH}} - \underset{\displaystyle CH_2-Cl}{\underset{|}{CH_3}}$

10. Cis + Antiaddition → Racemic mixture

11.



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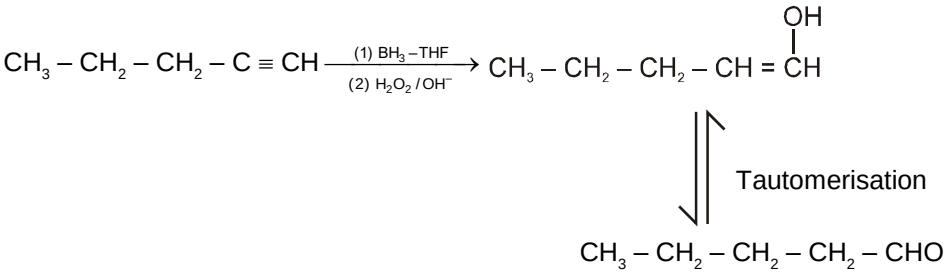

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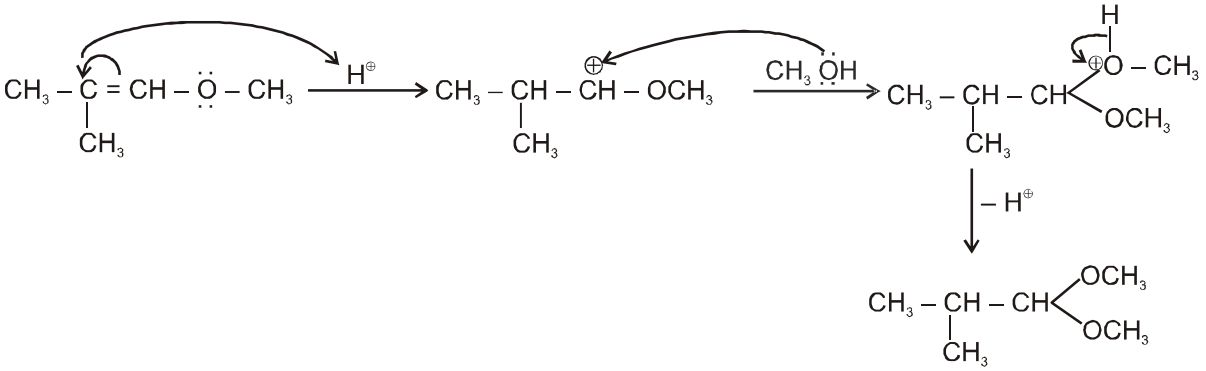

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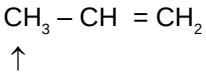
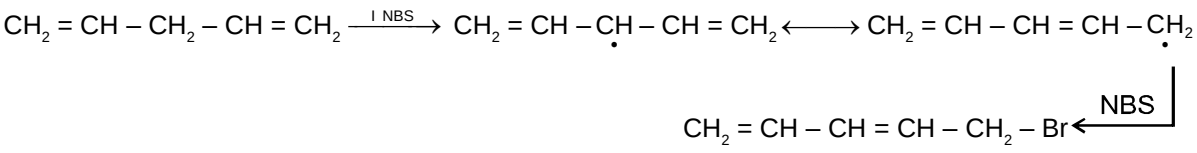


(1) Free radical site for Reaction

(2) Alkane like character

16.



17.

(1) $CaC_2 + H_2O \longrightarrow HC{\equiv}CH + Ca(OH)_2$

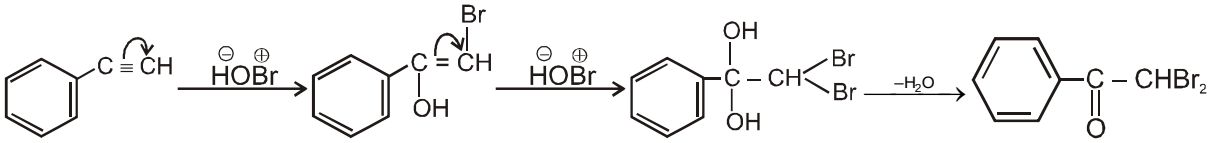
(2) $Mg_2C_3 + H_2O \longrightarrow CH_3{-}C{\equiv}CH + Mg(OH)_2$

(3) $Al_4C_3 + H_2O \longrightarrow CH_3{-}C{\equiv}CH + Al(OH)_3$

(4) $Cu_2Cl_2 + H_2O \longrightarrow 2Cu(OH) + 2HCl$

19. $CHI_3 + Ag + CHI_3 \longrightarrow HC{\equiv}CH + 6AgI$

20.



EXERCISE # 3
PART - I

7. $CH_3CH_2–C\equiv CH + HCl \longrightarrow CH_3-CH_2-\underset{\underset{Cl}{|}}{C}=CH_2 \xrightarrow{HI} CH_3CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{I}{|}}{C}}-CH_3$

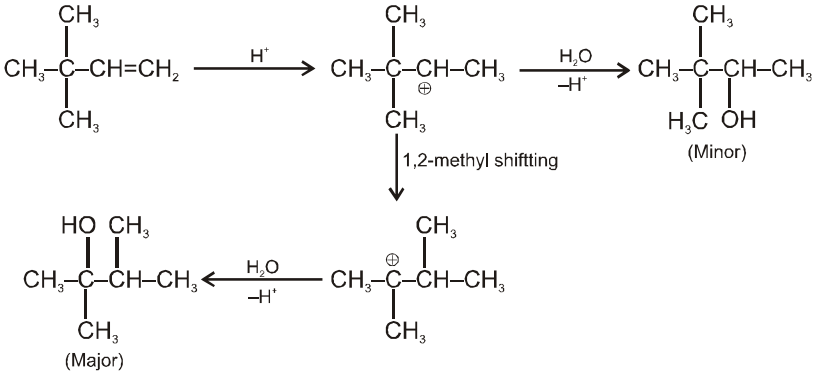
2-chloro,2-iodobutane

10. Electrophiles are electron deficient species. Among the given, $H_3O^{\oplus}$ has lone pair of electrons for donation, thus it is not electron deficient and hence, does not behave like an electrophile.

11. $CH_3–C \equiv C – CH_3$ (linear)

12. (1) Electrophilic addition (2) Nucleophilic addition
(3) Nucleophilic Substitution (4) Nucleophilic addition

13.



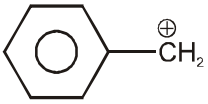
14. 1-Butyne and 2-butyne are distinguish by $NaNH_2$ because 1-Butyne react with $NaNH_2$ due to active hydrogen.

15. In Ethyne (CH≡CH) both carbon atoms are sp hybrid as the hybridisation of combustion product, carbon atom of O=C=O (CO_2).

16. $CH_3CH_2CH=CH_2 \xrightarrow[H_2O_2]{HBr} CH_3CH_2CH(Br)-CH_2 \xrightarrow{C_2H_5ONa} CH_3–(CH_2)_3–O–CH_2CH_3 \quad CH_3–(CH_2)_3–OCH_2CH_3$

HBr in presence of peroxide gives anti Markovnikoff addition product.
1ºalkyl halide on reaction with C_2H_5ONa gives S_N2 reaction.

17. $CH_3—CH=CH—CH_2—Cl \longrightarrow CH_3—CH=CH—\overset{\oplus}{C}H_2 \longrightarrow CH_3—\overset{\oplus}{C}H—CH=CH_2$

18. $CH_3—\overset{CH_3}{\underset{CH_3}{C}}\oplus$ is more stable than 

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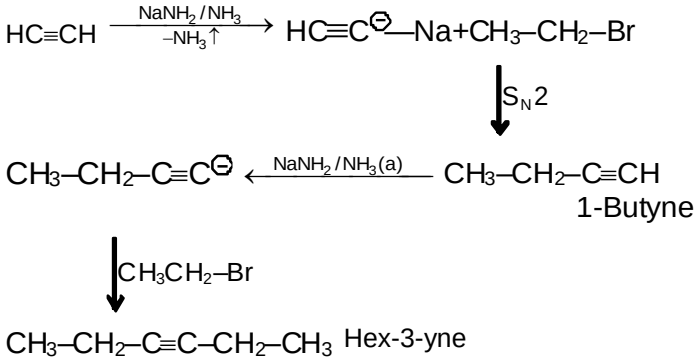
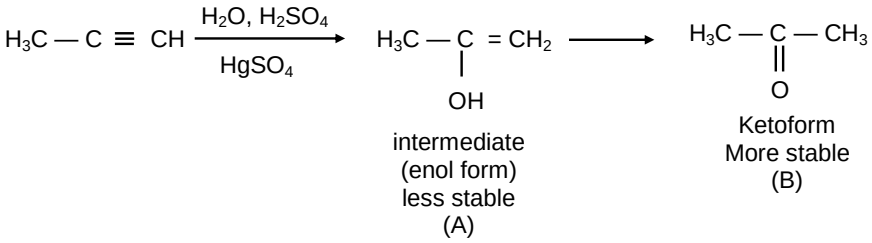
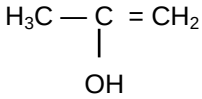
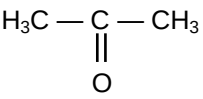




20.

So, A is  and B is 

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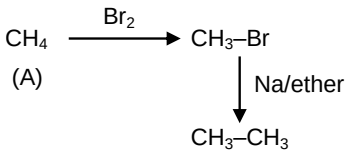
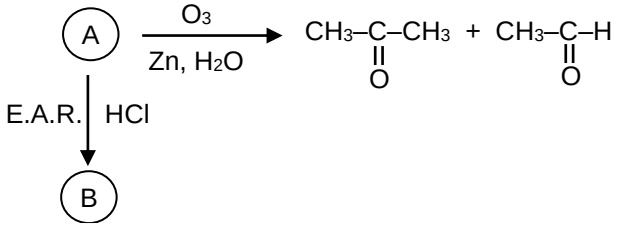
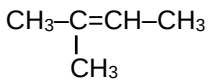


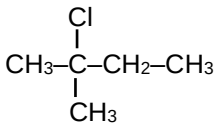
A is CH_4

B is $CH_3–CH_3$

22.



A = 

B = 

Formation of B from A is Markonikoff rule addition by E.A.R. mechanism

23. (i) $V_2O_5 = 2SO_2 + O_2 \xrightarrow{V_2O_5} 2SU_3$ MFG of H_2SO_4

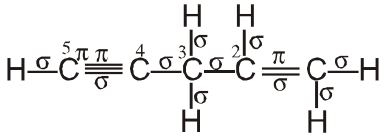
(ii) $TiCl_4 + Al(CH_3)_3$ = Polymerisation of Ethylene.

(iii) $PdCl_2$ = The oxidation of Ethyne to ethanol.

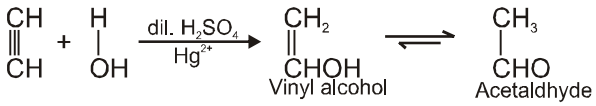
(iv) Ni Complex = Polymerisaton of Alkyne

PART - II

4. Pent-1-en-4-yne contain 10σ and 3π bonds.



5. Acetylene with dil. H_2SO_4 in the presence of Hg^{2+} ion forms aldehyde.



Note : Hydration of ethyne yields aldehyde but hydration of higher homologous of alkyne yields ketone.

6. Propanol-1 can be prepared from propene as follows :

$$CH_3CH = CH_2 \xrightarrow{B_2H_6} (CH_3CH_2CH_2)_3\,B \xrightarrow{H_2O_2/OH^-} \underset{\text{1- propanol}}{CH_3–CH_2–CH_2–OH}$$

$$CH_3CH = CH_2 \xrightarrow[dil.H_2SO_4]{HOH} \underset{\text{2-propanol}}{CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3}$$ (This addition follow Markownikoff's rule)

7. The addition of HBr on unsymmetrical alkene take palce on the basis of Markownikoff's addition.

$$\underset{\text{3-phenylpropene}}{C_6H_5CH_2–CH = CH_2} \xrightarrow{\overset{+\ -}{HBr}} C_6H_5CH_2–\overset{+}{C}H–CH_3 \xrightarrow{\text{1, 2 hydride shift}} C_6H_5\overset{+}{C}H–CH_2–CH_3$$

$$\xrightarrow{Br^-} C_6H_5CH(Br)CH_2\,CH_3$$

12. In chain terminating step, activation energy does not require.

13. Lewisite is obtained when acetylene reacts with arsenic chloride.

$$CH \equiv CH \xrightarrow{AsCl_3} \underset{\text{Lewisite}}{CHCl = CHAsCl_2}$$

14. (1) Pent-4-ene-1-yne

CH_2= CH–CH_2–C≡CH

No. of σ–bonds: 4 (C – C) + 6 (C – H) = 10

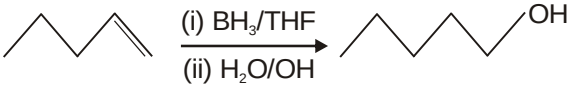
No. of π–bonds: 1 (C == C) + 2 (C ≡≡ C) = 3

15. Mass ratio of H : C = 1 : 12

However, given mass ratio of H : C = 1 : 3 Therefore, for every C atom, there are 4 H atoms, hence empirical formula = CH_4.

16. CH_4 has only one carbon atom, hence it can't be prepared by Wurtz reaction, which involves two molecules of alkyl halide.

17. Hydroborartion - oxidation leads to anti-Markownikoff's hydration, thus



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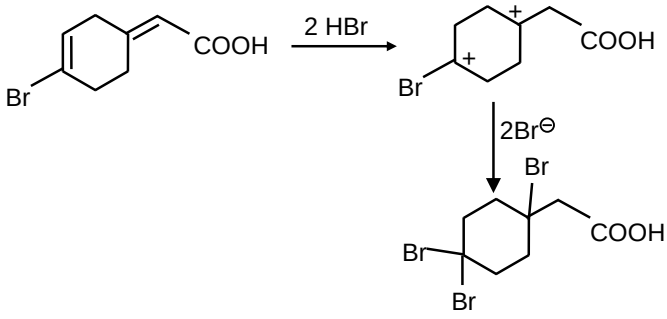
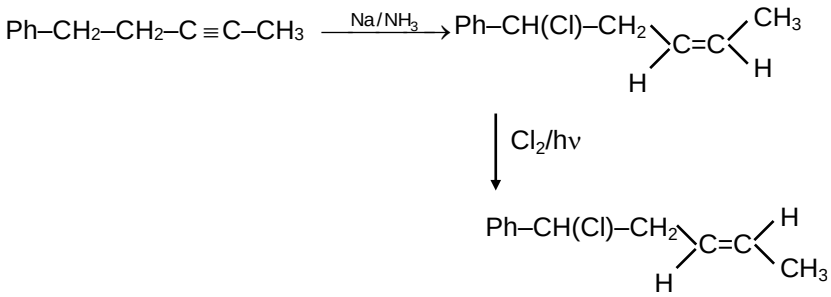


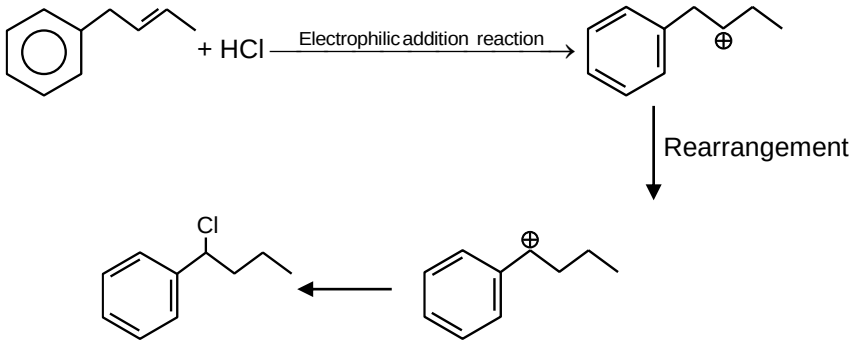
This is a electrohilic addition reaction reaction by markownikoff rule depond upon stability of carbocation.

21.



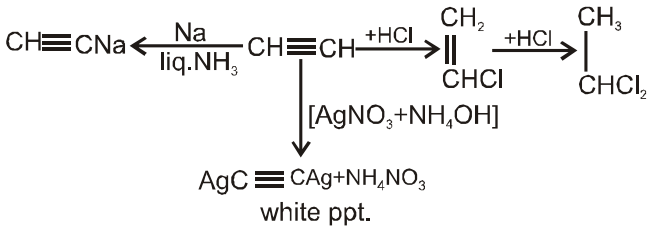
$Na/NH_3(l)$ this is Birch reduction reduce only alkyne into trans alkene and $Cl_2/h\nu$ is free radical substitution reaction

22.



PART - III

1. Acetylene reacts with the other three as :



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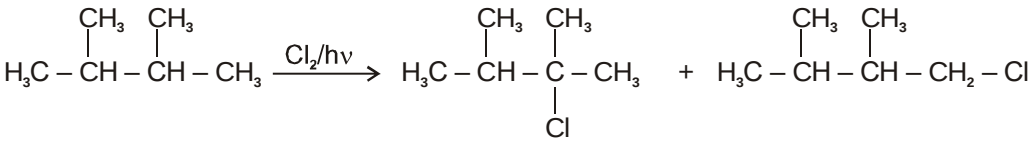


3. In Corey house synthesis of alkane, alkyl halide reacts with lithium dialkyl cuprate.

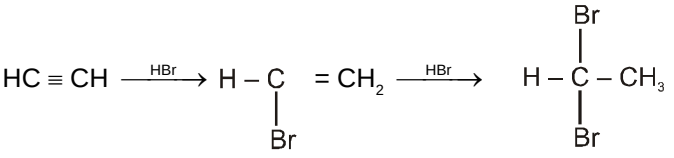
$R_2CULi + R'X \rightarrow RR' + RCu + LiX$

4. 1, 2-addition product is kinetically controlled product while 1, 4-addition product is thermodynamically controlled product and formed at comparitively higher temperature.

$$CH_2 = CH - CH = CH_2 \xrightarrow[40^\circ]{HBr} \underset{\text{1, 4–addition}}{CH_2(Br)\,CH = CHCH_3} + \underset{\text{1, 2–addition}}{CH_3\,CH(Br) - CH = CH_2}$$

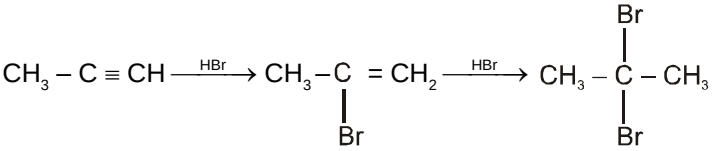
Therefore, 1 - bromo-2-butene will be the main product under themodynamically dcontrolled conditions.

5.



1,1 dibromoethane

2- bromopropane



7. $C_nH_{2n}O = 44$

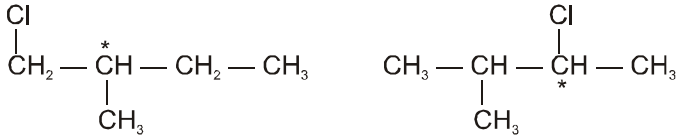
$C_nH_{2n} = 44 - 16$

$C_nH_{2n} = 28$

$n = 2$

$CH_3–CH=CH–CH_3 \xrightarrow{O_3/Zn} CH_3–CH=O$

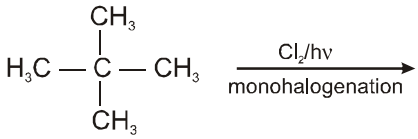
8.



(R + S) (R + S)

Four monochloro derivatives are chiral.

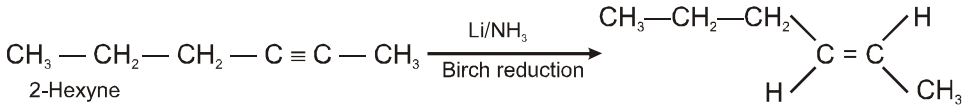
9.



neopentane

single product.

10.



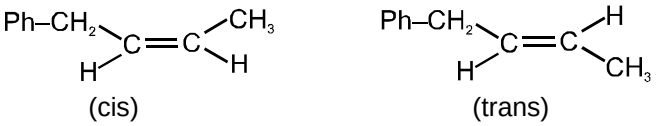
2-Hexyne

Trans-2-Hexene

11. $2CH_3–CCl_3 \xrightarrow[\Delta]{6Ag} \underset{\text{But-2-yne}}{CH_3–C \equiv C–CH_3} + 6AgCl$

12. Molecules with restricted rotation and having two different groups on both restricted atoms can show geometrical isomerism.

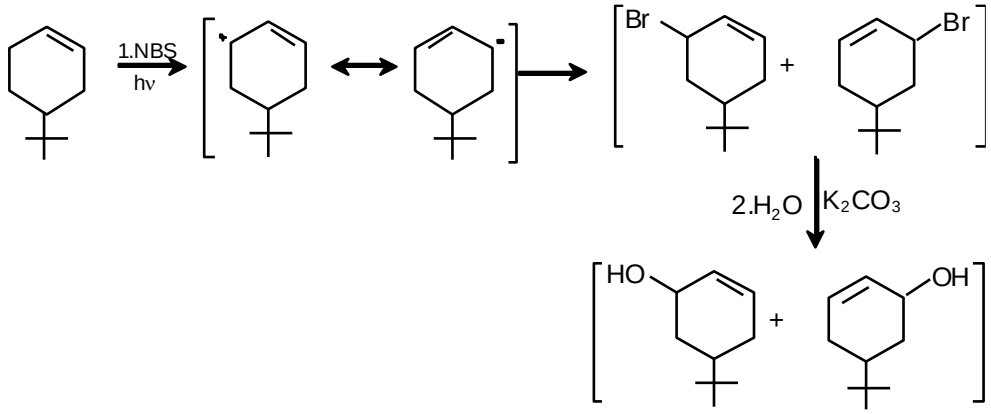
1 - Phenyl - 2- butene ($Ph–CH_2–CH=CH–CH_3$)



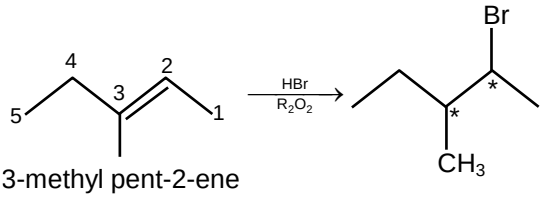
(cis) (trans)

13. $CH_3 - CH^+ - CH_2 - Cl$

14.



15.

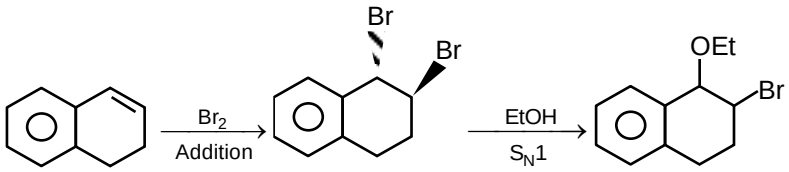


3-methyl pent-2-ene

Total stereo centers = 2, Total stereo isomers = 4

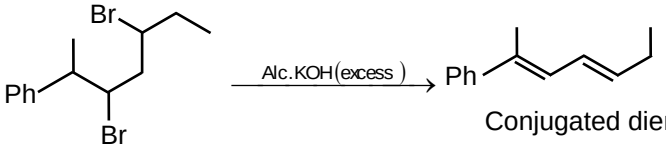
16. Na in liquid ammonia carryout anti and partial hydrogenation of alkyne to trans alkene.

17.



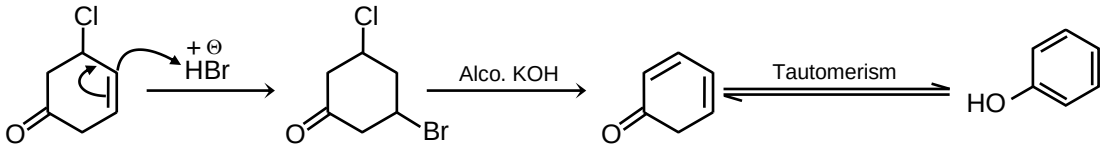
18. Allylic radical is more stable.

19.

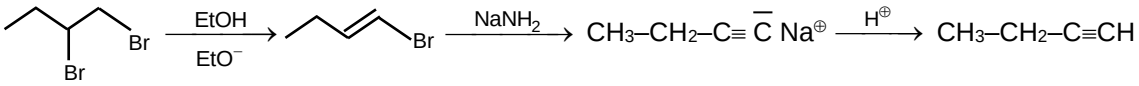


Conjugated diene

21.



22.



23.